

The Excitation of the Spectra of Nitrogen by Electron Impacts

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By D. C. DUNCAN

ABSTRACT

The excitation of the spectra of nitrogen was investigated by two methods: (1) in low-voltage arcs in a mixture of nitrogen and mercury vapor below the ionizing potential, and (2) in a three-element tube at low pressures.

The first, second, and fourth positive bands appeared below the ionizing potential, and are assigned to the neutral molecule. Three new low-potential systems are reported in the ultra-violet. These, also, are assigned to the neutral molecule. The third positive bands did not appear, and are probably due to a nitrogen oxide. The cyanogen bands were likewise absent.

The negative bands appear above the ionizing potential and increase in intensity with the degree of ionization, being emitted by the ionized molecule. New bands in the ultra-violet, degraded toward the red, appear simultaneously and, in addition to exhibiting a similar behavior, have the same Deslandres progression, indicating a physical relationship.

The line spectrum appeared above about 70 volts in ordinary arcs and as low as 35 volts in intense arcs, in agreement with the change in the rate of clean-up of nitrogen in the discharge.

Nitrogen has, in addition to a rich line spectrum, quite a number of band spectra, or band systems. Some of these systems have commanded considerable attention since the original work on the classification of band spectra, and, without a doubt, the same systems are destined to play a very important rôle in the future development of the theory of band spectra in general.

The principal band systems of nitrogen were originally classified

by Deslandres¹ as the first, second, and third positive groups and the negative group. This nomenclature was adopted in order to distinguish between those groups which, in the ordinary Geissler-tube discharge, appear with maximum intensity in the positive column and the group which appears with maximum intensity in the negative glow. These bands, in particular the second positive group and the negative group, served Deslandres quite admirably in arriving at the formulation of the laws which bear his name and in establishing the formulae which have played such an important part in the early theory of band spectra.

In addition, however, to these so-called Deslandres groups nitrogen has a number of other band systems. Some of these systems behave quite differently under given conditions of excitation. In fact, it is possible to excite some of these families without having the slightest trace of others.

Baly, as recently as 1912, in describing the primary and secondary spectra of hydrogen and other cases of so-called plurality of spectra writes:

These cases of plurality of spectra serve to show what an interesting field of work lies here; no explanation has yet been found of the curious facts described, and there is room for a great development of our knowledge in this direction.²

The years that have intervened have witnessed such a development, and our knowledge in this direction is increasing at a very rapid pace. It is now generally believed that the various separated divisions of the spectrum of a substance such as nitrogen may be attributed to the presence in the emitting source of molecules in various states of association, dissociation, and ionization, each type of molecule or atom giving rise to its own characteristic radiation.

The purpose of the present investigation was to excite the spectrum of nitrogen under such conditions as would permit one to determine, at least approximately, the minimum amount of energy required for the excitation of each of the several divisions of the nitrogen spectrum, and to study the behavior of these various groups of rays under different conditions of excitation. In this way it is possible, not only to assign each group to its proper emission

¹ *Comptes Rendus*, 100, 1259, 1885, *et seq.*

² Baly, *Spectroscopy*, p. 525.

center and to establish certain physical relationships between the groups, but, also, to gain some information relative to the several stages of excitation of a given emitter, the neutral molecule, for example, before and after the emission of the several divisions of the spectrum which are assigned to it.

With this in view, a spectrographic study was made of the radiations emitted by nitrogen gas when excited by electrons of known velocities. In the course of the investigation three somewhat different sources of radiation were used. During the early stages, a low-voltage arc maintained in nitrogen alone in a simple two-element, hot cathode tube served as the source of excitation. In order to use the arc as the source of radiation for accelerating voltages below the ionizing potential of nitrogen—it being impossible to maintain the arc in a diatomic gas much below the ionizing potential—mercury was introduced into the experimental tube and the relative pressures of mercury vapor and nitrogen gas regulated by temperature control. As a second source of radiation, the simple two-element tube was replaced by a three-element tube in which the grid and plate were connected to form the anode. The latter tube was provided with a quartz window through which the force-free region between the grid and filament could be projected, by means of a quartz lens, upon the slit of the spectrograph. The grid in this tube was distant about 0.7 cm from the filament, and the nitrogen pressures used extended over the range (0.6–0.003) mm.

Objection might be offered to these sources of radiation, as used, on the ground that the potential applied between the filament and the plate is not necessarily a measure of the velocity of the impacting electrons inasmuch as the electrons would undergo frequent collisions with gas molecules during transit from filament to plate, and consequently, might, in the two-element tube, reach the plate or, in the three-element tube, enter the force-free region between grid and plate with velocities varying anywhere from zero as a minimum to the applied accelerating potential as a maximum. To obviate this difficulty, a third experimental tube was used. The general form of this tube is shown in Figure 1. It consisted of a pyrex-glass tube about 30 cm in length and 5 cm in diameter, provided at either end with a hollow ground-glass stopper. One end carried the plate sup-

port, the other the filament leads and grid support. The grid in this case was a platinum gauze covering a small rectangular hole about 2×1 cm in the end of a cylindrical nickel shield inclosing the filament. The distance between filament and grid could be varied. This was made so small that, for the low pressures used, collision of electrons with gas molecules in this region was infrequent and it could safely be assumed that the electrons from the hot filament

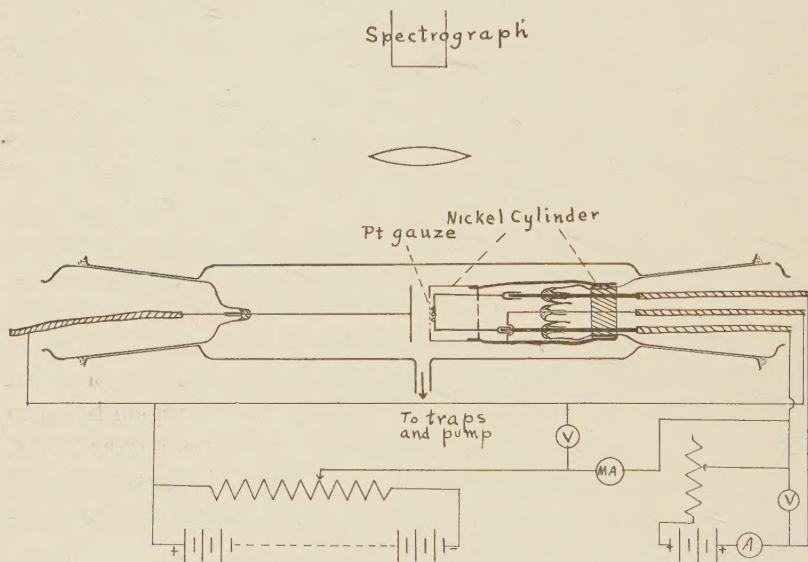


FIG. 1

entered the force-free region between grid and plate with a velocity equivalent of the accelerating potential applied between filament and grid.

Observations obtained using a source of radiation of this latter type agree very favorably with those obtained using experimental tubes of the two former types. This is to be expected if the theory of the low-voltage arc as developed by Duffendack¹ be a correct explanation of the phenomena. For if the redistribution of the electric intensity in the tube which accompanies the striking of the arc is such that practically the entire potential difference applied between

¹ *Physical Review*, 20, 668, 1922.

the electrodes is distributed over a space interval in the immediate vicinity of the cathode of the order of magnitude of the mean free path of an electron in nitrogen for the pressures used, then it is obvious that the electrons on first impact will have a velocity equivalent only slightly less than the applied potential difference. The successive excitation of the first two lines of the Balmer series at their radiating potential which has recently been reported by Duffendack¹ confirms this view.

The nitrogen used was prepared and purified by the method described by Waran.² Pure bromine water was dropped into pure ammonia solution. The nitrogen produced by the interaction was bubbled through a concentrated solution of *KOH* which served to remove any ammonia and bromine which might be mixed with the nitrogen. It was next passed through hot copper turnings to remove any traces of oxygen which may have come from dissolved air in the liquids, and then, prior to being admitted into the experimental tube, was stored in a compartment containing phosphorus pentoxide.

To make certain that some of the new bands observed were not due to impurities in the gas, several samples of nitrogen were used which had been prepared by slowly heating a mixture of sodium nitrite and ammonium sulphate. No differences, however, were observed on the spectrograms obtained from the nitrogen prepared by the two methods. Since these new band systems did not appear when the nitrogen was replaced by other gases, hydrogen and oxygen, it is safe to assume that they are due to nitrogen.

In preparing for each "run" the experimental tube was baked out for a period of six hours in an electric oven maintained at a temperature of 350° C. The pumps were operated continuously during this baking-out process. At frequent intervals during the last stages of baking, the filament was heated to a white heat, and nitrogen admitted and pumped out several times to get rid of any other occluded gases which might be present in the apparatus. The nitrogen used passed through a liquid-air trap just before entering the experimental tube. Pressures were measured with a McLeod gauge.

The low-voltage arc, as used in the greater part of this investi-

¹ *Op. cit.*, 23, 107, 1924; *Astrophysical Journal*, 60, 122, 1924.

² *Philosophical Magazine*, 42, 246, 1921.

gation, affords a very satisfactory source of excitation in that the energy of the impacting electrons can be readily controlled and measured, and, the arc being a region of very intense excitation, satisfactory spectrograms may be obtained with relatively short exposures.

Results.—Several series of spectrograms were obtained under different experimental conditions covering the spectral region $\lambda\lambda$ 7000–2000 Å. A careful examination of these spectrograms leads to some very definite information relative to the amount of energy required to excite each of the several divisions of the nitrogen spec-

TABLE I

Band System	End of Spectrum toward Which Bands Are Shaded	Excitation Potentials in Volts
First positive (Deslandres).....	More refrangible	9.5 $\pm$.5
Second positive (Deslandres).....	More refrangible	12.0 $\pm$.5
Fourth positive (Strutt).....	More refrangible	15.0 $\pm$.5
Fifth positive.....	More refrangible	10.0 $\pm$.5
Sixth positive.....	More refrangible	15.5 $\pm$.5
Seventh positive.....	Less refrangible	12.0 $\pm$ 1.0
First negative (Deslandres).....	More refrangible	18.0 $\pm$.5
Second negative.....	Less refrangible	18.5 $\pm$.5
3464.....	More refrangible	15.0 $\pm$.5
3021.2.....	Less refrangible	13.0 $\pm$.5

trum within the region studied. This information, together with the knowledge acquired from a study of the behavior of each group of rays under different physical conditions, should make it quite possible to predict the probable origin of each of these several groups.

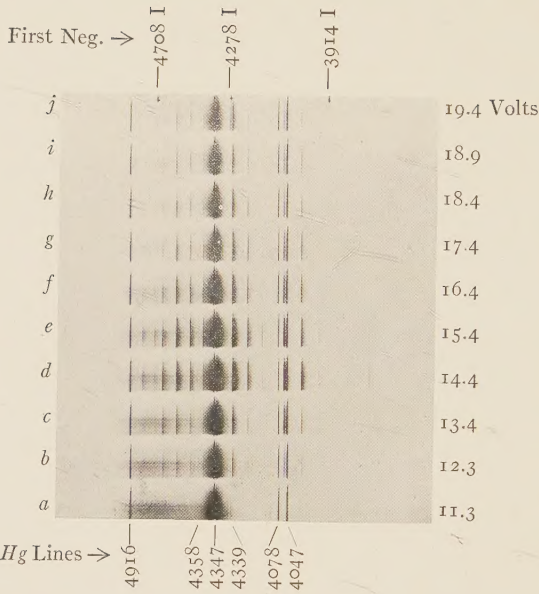
The band spectrum of nitrogen within this particular spectral range apparently comprises, in addition to the first, second, and fourth positive bands and the negative band systems which have been previously ascribed to it, at least four other groups or systems which are designated in this paper, for reasons that will appear later, as the fifth, sixth, and seventh positive systems, and the second negative band system. Also, there are two individual bands, one with head at 3464 Å, and the other with head at 3021 Å. These several band systems with their direction of shading and corresponding excitation potentials are given in Table I.

First positive group.—This system, part of which appears on

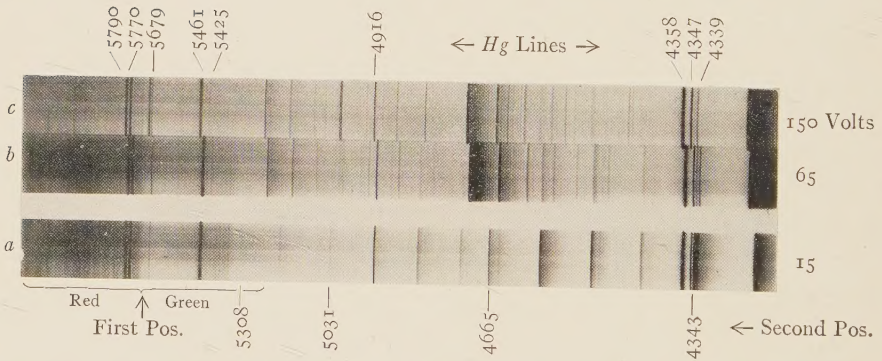
ERRATA: The second negative, and fifth and seventh positive bands reported herein as new nitrogen systems have been found to be due to carbon monoxide. Their excitation is now being investigated at the University of Michigan. In plate IC the wave lengths are printed in reverse order and so are improperly placed in the figure.—Jan. 4, 1926.

PLATE I

A



B



C

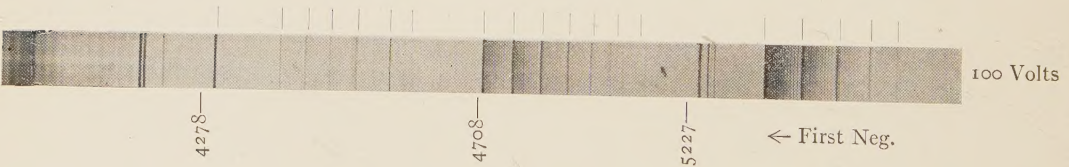


Plate I A, B, begins at about λ 9100 and extends over the greater portion of the visible spectrum. It comprises three more or less separate groups of bands—red, yellow, and green, respectively. While this system was not fully developed until the impacting electrons had attained a velocity equivalent of 12.5 volts, the principal components appeared at 10 volts. A twelve-hour exposure at 9 volts bore no trace of these bands, but they appeared, although quite faintly, on a three-hour exposure at 10 volts. The behavior of this system under different physical conditions has been variously reported on by Rayleigh, Lewis, and others. Fowler and Strutt,¹ while investigating the spectrum of the nitrogen afterglow, were led to the conclusion that the remarkable red, yellow, and green bands in the afterglow spectrum, originally observed by Lewis,² were a selection of the first positive nitrogen band system. In a more recent work Rayleigh³ has shown that the particular selection can be greatly modified by admixture of the inert gases, the effect of adding an inert gas being to shift the maximum of intensity in each group toward the red. Addition of helium in particular made the red group, as a whole, more intense at the expense of the others. In the present investigation the relative intensities of the three divisions did not change appreciably as the conditions of excitation were altered. Change of pressure, current, or voltage had no noticeable effect on the appearance other than to alter the intensity of the group as a whole. This, for a given current, appeared to reach a maximum at about 15 volts.

Second positive group.—This begins in the violet and extends to about λ 2800. The bands in this system, as seen from Plate I (A, Ba) and Plate II (A, B), have their heads toward the red end of the spectrum. The band heads are gathered in groups of five; except toward the head of the system where there is a group of two bands, then one of three, one of four, and finally the sequence of fives. It is of interest to note in passing that, on all of the spectrograms obtained, the last two members of the group with head at λ 3577 are greatly suppressed. The strongest members of this system appear faintly at

¹ *Proceedings of the Royal Society, A*, 85, 377, 1911.

² *Astrophysical Journal*, 20, 49, 1904; *Philosophical Magazine*, 25, 826, 1913.

³ *Proceedings of the Royal Society, A*, 102, 453, 1923.

12 volts, and the entire system develops shortly after this, reaching a maximum between 14 and 15 volts, as may be seen by reference to Plate I A. This spectrogram was obtained using as source of radiation a low-voltage arc in a mixture of nitrogen and mercury vapor in a simple two-element tube. It shows, consequently, in addition to the second positive bands, all the prominent mercury lines in this region of the spectrum. Also, the exposures at the three higher voltages show the coming in of negative band heads to which reference will be made later.

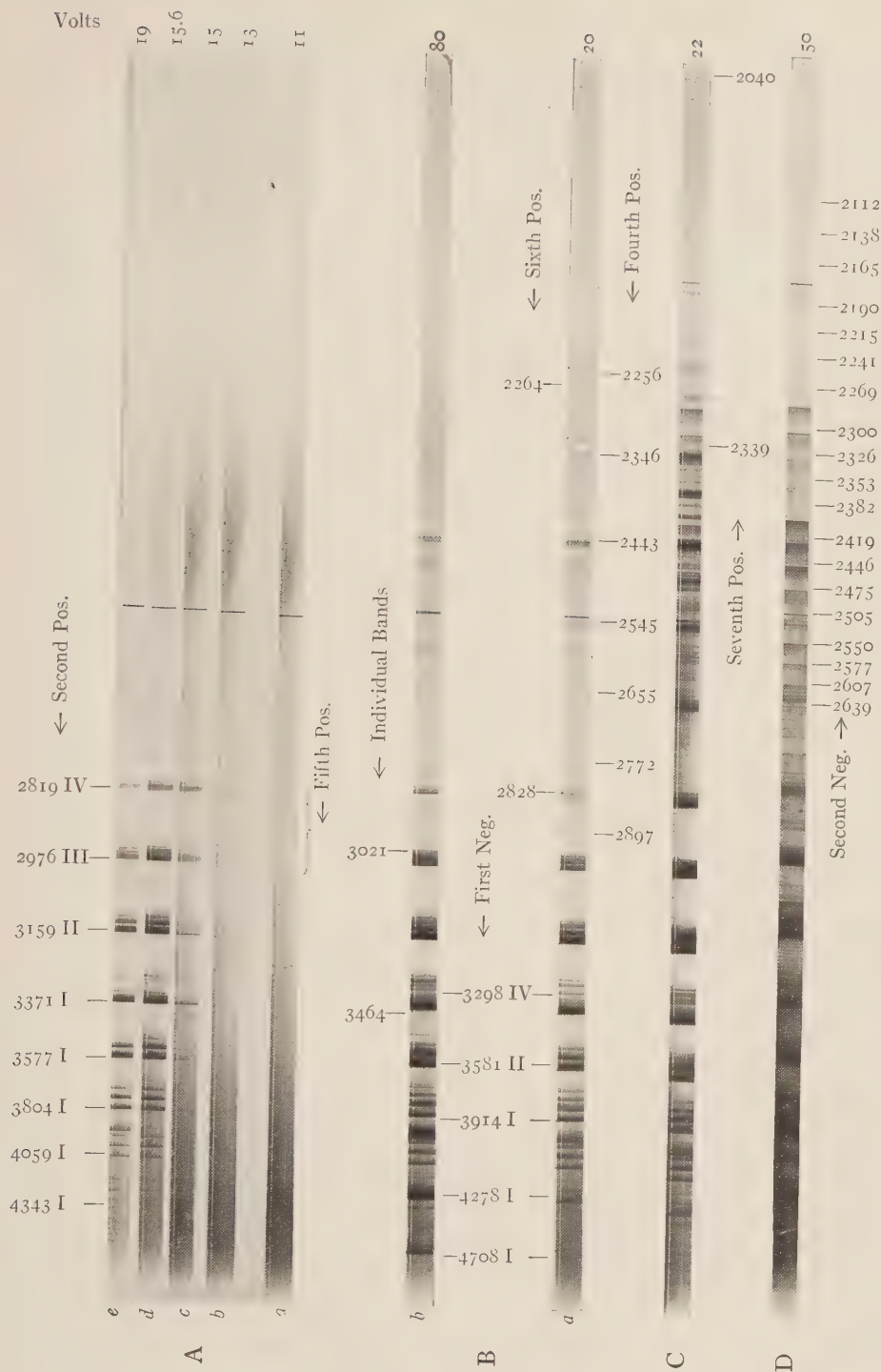
Plate II A was obtained by photographing the radiation from a three-element tube containing nitrogen alone. This particular series of spectrograms is shown merely to call attention to the presence of the chief members of the several groups on the 13-volt exposure with no evidence of the weaker members of these groups. It should not be inferred from the appearance of these spectrograms that the intensity of the second positive bands increases with increasing accelerating voltage. The exposures at the two higher voltages were taken after the striking of the arc, and the marked increase in the intensity of the bands here is due not so much to the increase in the voltage as to the enormous increase in the electron stream accompanying the striking of the arc.

Fourth positive group.—This system, shown on Plate II B, was originally reported by Fowler and Strutt.¹ It consists of seven groups extending over the region $\lambda\lambda$ 2900–2250. Each group comprises five principal heads of which the most refrangible is the strongest in each case. This system appears first faintly at 15 volts. The intensity increases slightly at first with the accelerating potential, reaches a maximum for about 20 volts, and then decreases with further increase in voltage.

Fifth positive bands.—This low-potential system appearing rather indistinctly on Plate II A, B, consists of two groups which bear a very striking resemblance to Strutt's fourth positive groups. Each group comprises four band heads of which the most refrangible is by far the most intense. The intensity of the other heads decreases with the degree of refrangibility, the two least refrangible heads being very faint. The behavior of these groups with increased volt-

¹ *Proceedings of the Royal Society, A*, **85**, 377, 1911.

PLATE II



age is not obvious from the spectrograms since they fall so close to the first two groups of the second positive system that they are soon shaded out by the latter. They apparently have the same critical potential as do the members of the first positive system. Appearing first faintly at 10 volts, they attain maximum intensity at about 20 volts. The series notation, wave-length, intensity, and corresponding wave-number for each of the band heads belonging to this system are given in Table II. The intensity is rated on a basis of 10 for the head of maximum intensity in this system.

It is quite apparent that this band system is closely related to the second and fourth positive systems, as may be seen by a con-

TABLE II
FIFTH POSITIVE BANDS

Series Notation	Wave-Length	Intensity	Wave-Number	Difference
I.....	2973.2	1	35,324	1704
II.....	2971.6	1	35,344	
III.....	2969.3	2	35,366	
IV.....	2968.2	5	35,394	
I.....	2830.9	2	33,633	
II.....	2829.3	2	33,652	
III.....	2827.8	6	33,677	
IV.....	2825.3	10	33,690	

sideration of their series relationships. In the first, third, and fifth columns of Table III are recorded the wave-numbers of the last two terms of the fourth series of the second, fourth, and fifth positive bands, respectively. The wave-number intervals, 82 and 83, between the corresponding terms in the first and third column are equal within the limits of error. The same is true of the differences 8916 and 8919 between corresponding terms of the fourth and fifth positive bands. Also the wave-number interval, 1704, for the strongest heads of this system, recorded in the last column of Table II, is equal, within the limits of error, to the corresponding intervals 1704 and 1705 between the last two terms of the fourth series of the second and fourth positive band systems, respectively. Numerically, at least, then, the fifth positive bands are related to the second and fourth positive bands.

Sixth positive bands.—This system, shown on Plate II B, extends over the region $\lambda\lambda$ 2828–2111. The general character of this group is quite different from that of the groups described above, as may be gained from the plates. Series relationships for this and the next succeeding system have not been established as yet. Appearing

TABLE III

Second Positive Series IV	Difference	Fifth Positive Series IV	Difference	Fourth Positive Series IV
33,77 ²	82	33,690	8916	42,606
35,477	83	35,394	8919	44,313

first at 15.5 volts, this system increases in intensity with increased voltage, attaining a maximum of intensity at approximately 20 volts. Further increase in accelerating potential has only very slight effect on the appearance of the groups. The wave-lengths for the bands of this system, and their approximate intensities on a scale of 10 for the strongest, are given in Table IV.

TABLE IV
SIXTH POSITIVE BANDS

Wave-Length	Intensity	Wave-Length	Intensity
2828.1	7	2431.6	2
2743.3	2	2418.0	1
2722.5	8	2412.0	8
2696.0	1	2355.4	8
2682.0	3	2322.7	2
2647.0	1	2303.7	2
2636.5	3	2274.9	1
2625.0	8	2264.1	8
2596.2	1	2245.0	2
2587.0	9	2236.3	2
2556.4	2	2222.2	1
2523.1	5	2182.0	7
2497.5	10	2166.0	6
2470.5	9	2111.0	4

Seventh positive bands.—The strongest members of this low-potential system are shown on Plate II C. The spacing of the partial band components here is very similar to that for the system of bands in the Schumann region photographed by Lyman.¹ While

¹ *Spectroscopy of Extreme Ultra-Violet*, p. 113, 1914.

in no case did this system appear with sufficient intensity to be detected at less than 12 volts it is quite possible that its critical potential is a volt or more below this value. For not only does the extreme faintness of this system make the exact determination of its critical potential difficult, but it is quite possible that the bands having the initial state zero, which should be the first bands of the system to be excited, as will be seen from the later discussion, lie beyond the range of the spectrograph. Like the other positive bands described here, this system is of maximum intensity for moderate potentials of the order of 20 volts. The wave-lengths and approximate intensities of the band heads of this system are given in Table V.

TABLE V
SEVENTH POSITIVE BANDS

Wave-Length	Intensity	Wave-Length	Intensity
2338.7.....	3	2173.7.....	8
2312.4.....	5	2151.1.....	10
2286.7.....	8	2128.7.....	5
2247.5.....	4	2107.1.....	2
2221.9.....	4	2088.0.....	3
2209.0.....	1	2064.0.....	4
2196.6.....	5	2040.0.....	4

First negative bands (Deslandres).—According to the original classification by Deslandres, this system consists of six groups of five bands each, extending from λ 5227 to λ 3296 with several members missing from some of the groups. It is of interest to note that the group with head at 5227 Å for which only the first two components are reported in Kayser's *Handbuch der Spectroscopie* appears here with no less than seven bands, as may be seen from Plate I C. The low-voltage arc appears to provide a particularly favorable source for the excitation of the negative bands, for they become very intense at the higher voltages and show their fine structure. The bands of longest wave-length in the several groups appear first at 18 volts, as may be observed from Plate I A. It is significant that this is just above the ionizing potential of nitrogen (16.9 volts). With increasing accelerating potential the remaining members of the groups appear in order and the intensity of the entire system increases very markedly (Plate I B).

Second negative system.—The series classification, wave-lengths, approximate intensities, and corresponding wave-numbers for the bands of this system are given in Table VI.

It is suggested that this system be called the “second negative” in order to indicate the relationship, apparently very close, which exists between these bands and the negative bands of Deslandres just described. As may be seen from Plate II D, this system comprises five groups extending over the region $\lambda\lambda$ 2638–2112. Like

TABLE VI
SECOND NEGATIVE SYSTEM

Series	Wave-Length	Intensity	Wave-Number
IV.....	2638.6	4	37,899
III.....	2607.5	5	38,351
II.....	2577.5	5	38,797
I.....	2550.2	6	39,213
IV.....	2504.7	6	39,923
III.....	2474.6	8	40,410
II.....	2446.0	9	40,883
I.....	2419.2	10	41,336
IV.....	2382.5	2	41,972
III.....	2353.2	3	42,495
II.....	2325.3	5	43,006
I.....	2300.0	7	43,478
IV.....	2269.4	1	44,064
III.....	2241.0	1	44,622
II.....	2214.8	2	45,151
I.....	2190.2	6	45,658
IV.....	2165.0	1	46,189
III.....	2138.1	3	46,770
II.....	2112.5	5	47,335

the seventh positive bands, these bands are degraded toward the red end of the spectrum. Appearing first faintly at 18.5 volts, they undergo a very marked increase in intensity with increasing voltage. They have not only the same critical potential as the negative bands of Deslandres, but also identical series relationships, as may be seen from Tables VII and VIII.

The law governing the arrangement of the band heads in a band system, commonly known as the “second law of Deslandres,” states that each series is so arranged that the intervals between the frequencies of successive heads form an arithmetical progression, and further, that all the series in a given band system are exactly similar

and may be obtained one from the other by adding or subtracting a constant. The wave-numbers of the first four series of the first negative system and the four series of this new system are given in Tables VII and VIII, respectively. The differences between the consecutive terms of the several series are given in the fifth column in each case.

TABLE VII
FIRST NEGATIVE BANDS

Series I .	Series II	Series III	Series IV	Difference	Second Difference
25,545.....	27,917			2172	
23,370.....	25,746	28,060		2134	38
21,236.....	23,604	25,923	28,180	2110	24
19,129.....	21,491	23,809	26,073	2072	38
.....	19,423	21,734	23,998	2039	33
.....		19,699	21,954	2000	39
.....			19,954		
Average....					33

TABLE VIII
SECOND NEGATIVE BANDS

Series I	Series II	Series III	Series IV	Difference	Second Difference
45,658.....	47,335			2182	
43,478.....	45,151	46,770		2144	38
41,336.....	43,006	44,623	46,189	2124	20
39,213.....	40,883	42,495	44,064	2087	37
.....	38,797	40,410	41,972	2054	33
.....		38,351	39,923	2024	30
.....			37,899		
Average....					31

The average second difference, 33, of the first system is equal, within the limits of error, to the average second difference, 31, of the second system. These two systems then have the same Deslandres progression.

For the first negative system, the mean difference between series I and II is 2369, between series II and III it is 2315, and between series III and IV it is 2260. These differences also form an arithmetical series having an interval 54. This interval is identical with that of the series formed by the corresponding differences for the second nega-

tive bands. It is obvious, therefore, that the separate series of these two band systems are similarly constituted, and only differ from one another by a constant amount in each case. It will be seen from the discussion that follows that the fact that these two band systems have a common excitation potential and the same Deslandres progression makes it seem quite probable that they have the same initial state.

The individual bands, Plate IIBb, with heads at λ 3464 and λ 3021.2, respectively, do not appear to be related to any of the band systems already described. The former, with its edge toward the red, appears first at about 15 volts and becomes very intense at the higher voltages, its fine structure extending throughout the second positive group with head at λ 3371. The λ 3021.2 band is degraded toward the red, and has a slightly lower critical potential. It appears first at about 13 volts, but does not undergo any very marked change with increasing voltage.

Discussion.—As indicated above, these several band systems are affected quite differently by physical conditions. The majority of the systems described, as has been seen, appear at voltages considerably below the ionization potential of nitrogen. Moreover, these systems diminish in intensity as the accelerating voltage is increased above the ionizing potential; that is, as the relative number of excited neutral molecules in the emitting source decreases. The two negative systems, on the other hand, do not appear until the impacting electrons have a velocity equivalent greater than the ionizing potential. The intensity of each of these systems increases quite markedly as the voltage increases; that is, as the relative number of ionized molecules in the emitting source increases. The observed behavior, then, makes it seem quite probable that all of the systems here described, with the exception of the negative bands, are due to the neutral molecule; whereas the two remaining systems are due to the ionized molecule. These observations are in good agreement with those of other investigators in so far as experimental evidence is available. L. and E. Bloch,¹ using a three-element tube, were able to excite the second positive bands by electron impacts as low as 12 volts. Brandt,² using a four-element tube to investigate the ex-

¹ *Comptes Rendus*, **175**, 225, 1921.

² *Zeitschrift für Physik*, **8**, 32, 1921.

citation limits of the nitrogen molecule due to electron impacts, obtained numerous kinks in the current-voltage curve between 7.5 and 8.2. By applying the $h\nu$ -relation to these discontinuities he was able to construct a band which agrees in frequency difference with some of the observed positive bands. He found that the band character of these discontinuities continued beyond the ionizing potential of nitrogen, and concluded that the molecule can be ionized without dissociation. Fulcher,¹ while studying the spectra produced by low-potential discharges in air, noted that a decrease in the discharge potential was accompanied by a striking decrease in the relative intensity of the negative nitrogen bands with respect to the positive bands. Wien,² using the method of positive rays to determine whether certain radiations were due to charged or uncharged particles, found, in working with nitrogen, that the bands of the second positive group showed no displacement, whereas the negative bands were displaced. He concluded, therefore, that the former are due to neutral molecules whereas the latter are due to positively charged particles. Similarly, Steubing,³ in studying the effect of electric fields on the positive-ray spectra of nitrogen, found that the intensity of the negative bands was very materially decreased with the application of strong electric fields.

Referring again to Plate IA, B, we note the behavior of the second positive and the first negative bands under varying velocities of impacting electrons. The second positive bands appear faintly at about 12 volts, increase in intensity with the voltage, reaching a maximum at about 15 volts, and then decrease with further increase in voltage; that is, they decrease in intensity as the degree of ionization in the tube increases. Figure 1 also shows the coming in of the negative band heads 4708, 4278, and 3914 at about 18 volts. This is just a little above the ionizing potential of nitrogen. These bands, also the bands of the second negative system, Plate II D, increase in intensity very markedly with increased voltage; that is, with the degree of ionization in the tube.

All of these observations support the conclusion that the systems

¹ *Astrophysical Journal*, 37, 61, 1913.

² *Annalen der Physik*, 69, 5, 325, 1922.

³ *Zeitschrift für Physik*, 23, 427, 1922.

designated here as positive are due to the neutral molecule, in various stages of excitation, whereas the negative bands are due to the ionized molecule.

The so-called third positive bands of nitrogen did not appear on any of the spectrograms. It is singular that any radiation due to the molecule should fail to appear when the known systems show so strongly and other systems, previously unknown, are excited. This non-appearance, then, of the third positive bands confirms the belief that they are not due to nitrogen alone but to some compound of nitrogen, probably an oxide, as is generally believed. Likewise, the absence of the cyanogen bands which have been variously attributed to the nitrogen molecule, but whose origin has been the source of much controversy, makes it appear as if they too are due to a carrier other than nitrogen. This supports the view of Barrett,¹ Rayleigh,² and Birge.³

The line spectrum of nitrogen, Plate I Bc, only appeared for accelerating potentials above about 70 volts in moderate arcs, but could be detected as low as 35 volts in very strong arcs. This is in agreement with the observations by Compton and Duffendack⁴ on the variation of the rate of clean-up of nitrogen with the voltage in low-voltage arcs. They observed a decided increase in the rate of clean-up at about 70 volts, but they also found quite an appreciable decrease in pressure in the tube when the arc was operating at potentials as low as 35 volts. This would indicate that dissociation does occur in the arc, but that the amount of dissociation is relatively slight until the impacting electrons have acquired a velocity equivalent of the order of 70 volts.

It is difficult to account for the non-appearance of the lines in moderate arcs at less than 70 volts. Apparently, it is impossible to dissociate a nitrogen molecule and ionize one of the atoms at a single impact. On the other hand, it is quite probable that there is a line emission at the lower voltages in moderate arcs corresponding to the slight amount of dissociation present, but that the emission is so faint that the lines are shaded out by the more intense band spec-

¹ *Proceedings of the Royal Society, A*, **98**, 40, 1921.

² *Ibid.*, *A*, **102**, 455, 1923.

³ *Physical Review*, **23**, 295, 1924.

⁴ *Ibid.*, p. 109, 1924.

tra which extend over the greater part of the photographic plate. The lines could be photographed as low as 35 volts in very strong arcs obtained by introducing metallic magnesium into the tube.

Although the theory of band spectra is as yet far from being as firmly established as that of line spectra, there is now little room for doubt that the general method of attack which, as developed by Bohr, has proved so fruitful in the explanation of line spectra, will prove equally effective in the field of band spectra. Here, however, instead of the emission (or absorption) frequency being determined by the change in energy occurring when the atom changes from one stationary state to another as a result of the shift of an electron from one stationary orbit to another, we have a much more complicated process. Sommerfeld,¹ in his excellent treatment of the theory of band spectra, as developed by Heurlinger, Swarzschild, Lenz, and others, points out that the most general type of band spectrum may comprise several band systems of the type described in this paper. Such a band spectrum results from energy changes of three different types occurring simultaneously in molecules. Each line in a band corresponds to a particular transition in the rotational energy of the molecule, each band in a system to a given change in the vibrational energy, and finally each system is due to a specific electron transition.

We are interested here, not in the line structure of the bands, but rather in the position of the various bands that make up a system and the relations between the several systems. According to the suggestion of Heurlinger and Lenz, the different bands, usually associated in a group, are due to changes in the vibrational energy of the molecules. The nuclear vibrations are quantized just as are the molecular rotations. But, whereas at normal temperatures, the molecules of the simpler gases, as indicated by their thermodynamic behavior, do not possess appreciable vibrational energy, or, in terms of stationary states, are in their zero vibrational state, they do in general possess rotational energy.

When energy is absorbed by a gas molecule, whether it be radiant energy or energy of collision, there results in the most general case a change in the rotational and vibrational state as well as in the elec-

¹ *Atombau und Spektrallinien*, chap. vii.

tron configuration. When the molecule returns to its normal state, possibly through a series of intermediate states, it will give up this energy in the form of radiation. The frequency of the radiation emitted by any particular molecule at a particular instant is then given by the quantum-relation $\Delta E = h\nu$, according to the second postulate of Bohr; where now ΔE represents the difference between the energies associated with those two states of the molecule between which transition has taken place and is really the algebraic summation of the energy changes occurring simultaneously in the three transitions indicated above. The wave-number, then, of any line in a band spectrum is given by an expression of the form

$$r = F'(e', n', m') - F(e, n, m), \quad (1)$$

where e' , n' , and m' are quantum-numbers characterizing the initial state of the electron configuration, the nuclear vibration, and the molecular rotation, respectively, and e , n , and m are numbers characterizing the same quantities after the emission of the radiation in question. This expression when applied to the null lines, that is the lines corresponding to the rotationless states in a given band system, has been shown by Heurlinger¹ to take the form

$$r = r_e + (a'n' + b'n'^2) - (an + bn^2), \quad (2)$$

where r_e is, for the most part, the contribution to the wave-number of the emitted radiation corresponding to the change in the electronic energy and a' , b' , and a , b , are coefficients characteristic of the law of force between the nuclei in the initial and final states of vibration, respectively. The zero line of a band is in general not far distant from the head or edge of the band. So that, whereas the wave-number given by equation (2) corresponds strictly to the zero line of the band, it may be regarded as corresponding approximately to the band edge. Corresponding to a definite quantum-jump, $n'-n$, we get for different values of n' (or n) a series of bands, or zero lines that are neighbors within the same band system. These bands constitute a band group. The emission, then, of each member of a given group is associated with the same vibrational quantum-jump. Thus, for the first negative system, Plate I C and Plate II B,

¹ *Zeitschrift für Physik*, 1, 82, 1920.

the groups with heads at 3298, 3581, 3914, 4278, 4708, and 5227 correspond to vibrational quantum-shifts of +2, +1, 0, -1, -2, and -3 units, respectively. The several members of a group differ in that they are associated with different initial, and therefore different final, states of vibration. Thus, the members of the group with head at λ 4708, corresponding to a quantum-shift $n' - n = -2$, are due to quantum-shifts $0 \rightarrow 2$, $1 \rightarrow 3$, $2 \rightarrow 4$, etc. Bands whose emission is associated with a common initial state but with different final states of vibrational energy have wave-numbers which are related through a Deslandres progression; thus we have the several series of bands in each band system. Moreover, as Sommerfeld points out, if it happens that two electron transitions that give rise to two different band systems have either the initial state or the final state in common, these systems will be closely related. This is true of the two negative band systems described above. The fact that these two systems have the same critical potential and also the same Deslandres progression is evidence, as pointed out earlier in this paper, that they have the same initial state. Furthermore, the series relationships of the first, second, fourth, and fifth positive systems indicate that they too are associated with a common state. Birge,¹ from empirical considerations, has been led to the conclusion that the second and fourth positive bands have a common final quantum-state and that this state is also the initial state of the first positive group. In assigning quantum-numbers to the bands of these systems, he has shown that the bands with heads at λ 9108 and λ 3371 correspond to the quantum-shift $0 \rightarrow 0$ in the first and second positive systems, respectively. This is in good agreement with the experimental results obtained in the present investigation. Referring again to Plate IIA, we note the gradual development of the second positive system as the energy of the impacting electrons is increased. It can be seen that the group with the head at λ 3371 is of maximum intensity and that the whole system develops symmetrically about this group. In fact, it appears to be generally true that the band of maximum intensity in a system is the one which corresponds to the quantum-shift $0 \rightarrow 0$. But, since the intensity of any particular band is proportional to the frequency of occurrence of the

¹ *Physical Review*, **23**, 294, 1924.

corresponding quantum-shift, and of the original state, we may conclude that the more probable quantum-shifts are those corresponding to the lesser values of $(n'-n)$, and in particular to the least value of n' .

It will be recalled that the first positive bands appeared first for an accelerating potential of 10 volts. However, since the $0 \rightarrow 0$ band at λ 9108, which should be the first of this system to be excited, was considerably beyond the range of the spectrograph used, it is quite probable that the critical potential of this system is as low as 9.5 volts. This, then, is 2.5 volts less than the critical potential found here for the second positive system. Applying the hr -relation to the bands λ 9108 and λ 3371, the $0 \rightarrow 0$ bands of the first and second system, respectively, we find that the energy associated with the radiation λ 3371 is greater than that associated with λ 9108 by an amount equivalent to 2.3 volts. This is in even better agreement with the experimental value 2.5 volts than might reasonably be expected, since, as pointed out above, the value 9.5 volts, taken as the excitation potential of the first positive system, is really an estimate based on the manner in which the various systems develop with increasing potential. An exposure at 9 volts showed no trace of these bands while at 10 volts they appeared fairly well developed.

The fact that the excitation voltage of each of the band systems photographed in this investigation is much higher than one would obtain by applying the hr -relation to the $0 \rightarrow 0$ band of the given system indicates that the molecule is not returned to the normal state by the emission of any of these systems. The absence of corresponding absorption bands in this region is in agreement with this view. In unexcited nitrogen there should be absorption corresponding to the transition of the molecule from the normal to an excited state. There is no record of absorption in the spectral region studied. According to Schumann,¹ nitrogen is very transparent even beyond λ 1650. Lyman² found a slight absorption extending from λ 1800 to λ 1250. In a later work³ he extended the emission spectrum to about λ 975, where it came to an end rather sharply, suggesting the possi-

¹ *Annalen der Physik*, 6, 418, 1901.

² *Spectroscopy of Extreme Ultra-Violet*, p. 63.

³ *Astrophysical Journal*, 43, 89, 1916.

bility of strong absorption beyond this point. It is quite obvious, then, that there must be other bands in the far ultra-violet, the emission of which corresponds to the return of the molecule to the normal state from that state in which it is left after the emission of the band systems studied here. Possibly the emission of the bands photographed by Lyman,¹ or the A bands, reported by Hopfield,² constitute the last stage in the return of the molecule to the normal or unexcited state.

It is to be hoped that measurements such as reported in the present paper of the amount of energy required to bring the molecule to each of the several stages of excitation corresponding to the emission of each of the several band systems may play the same important rôle in developing ideas of molecular structure and confirming the theory of band spectra as have the corresponding measurements on electron-atomic collisions in confirming and extending the general theory of atomic structure and line spectra as developed by Bohr.

SUMMARY

1. An account is given of the experimental determination of the various energy levels of the nitrogen molecule which are associated with the emission of radiation within the spectral region $\lambda\lambda$ 7000–2000. As many as six energy levels are established for the neutral molecule whereas only one, with a possibility of a second separated from the first by less than a volt, is found for the ionized molecule.

2. A study is made of the behavior of the several band systems with increasing energy of excitation, and it is shown that the development of the several systems is consistent with the present views of band spectra.

3. Arguments are presented for assigning certain band systems to the neutral molecules and others to the ionized molecule.

4. New bands in the negative band system are reported so that the system is now symmetrically developed.

5. The first, second, and fourth positive bands are shown to be due to the neutral molecule. Three new band systems, likewise due to the neutral molecule, are reported.

¹ *Spectroscopy of Extreme Ultra-Violet*, p. 113.

² *Physical Review*, **20**, 573, 1922.

6. A new band system is reported which is shown to have common series relationships with the negative bands of Deslandres. Each of these systems is assigned to the ionized molecule.

7. Comparison of the measured critical potentials with the voltage, as calculated by the energy equation, $Ve = h\nu$, corresponding to the frequency of the $\text{O} \rightarrow \text{O}^+$ band for each of the several band systems, shows that the emission of none of the band systems studied returns the molecule to the normal state, and hence leads to the prediction of a relation between these bands and a system, or systems, in the extreme ultra-violet.

8. The failure of the third positive nitrogen bands and the cyanogen bands to appear is offered as additional evidence that these bands do not belong to nitrogen.

9. It is shown that the intensity of the nitrogen line spectrum is associated with the rate of disappearance of the gas from the discharge tube and hence dependent upon the degree of dissociation.

The experimental work in connection with this investigation was carried out at the University of Michigan. The writer wishes hereby to express his gratitude to Dr. O. S. Duffendack for his many valuable suggestions and keen interest in the work; also to Professor H. M. Randall, director of the Physics Laboratory, for securing the necessary apparatus and equipment. The writer wishes, furthermore, to acknowledge indebtedness to the Palmer Physical Laboratory for the use of the large Hilger quartz spectrograph.

PENNSYLVANIA STATE COLLEGE
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DESCRIPTION OF PLATES

PLATE I

A. The second positive bands appear first in (*b*), reach maximum intensity at about 15 volts, and then fade out with increased voltage. The three chief heads 4708, 4279, and 3914 of the negative band system appear first in (*h*) and increase in intensity with increased voltage.

B. (*a*) Those portions of the first and second positive band systems that lie within this spectral region appear fully developed at 15 volts. This spectrogram shows no trace of the negative bands. (*b*) First and second positive bands with

faint trace of line spectrum. Negative bands are here very intense. (c) Line spectrum here fully excited and negative bands even more intense than at 65 volts.

C. The negative groups with heads at 5227, 4708, and 4278 highly developed with seven, seven, and five bands, respectively.

PLATE II

A. (a) The two groups of the fifth positive system appear here at 11 volts.

(b) The chief components of the second positive system are present at 13 volts. The weaker components of this system appear at the higher voltages.

B. The several bands and band systems labeled here are two bands with heads at 3464 and 3021, respectively; the fourth and sixth positive bands; and the first negative bands. Only the chief components of the groups are labeled.

C. Some of the members of the seventh positive system appear on this spectrogram.

D. The second negative system, of which only the chief components are labeled, is shown fairly well developed.

